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Research and Development Technical Report

DELET-TR-0420-3

STUDIES LEADING TO THE DEVELOPMENT OF HIGH-RATE LITHIUM-SULFURYL CHLORIDE BATTERY TECHNOLOGY

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The overall aim of the program is an examination of the viability of an active electrolyte lithium-sulfuryl chloride battery system. The specific objectives are;

- o Quantify the stability of lithium in sulfuryl-chloride based electrolyte.
 - Develop means to stabilize in the lithium anode in sulfuryl chloride based electrolyte to meet Army storage requirements.
- Establish the performance limits of $\text{Li/SO}_2^{\text{Cl}_2^{\text{T}}}$ cells with respect to cathode and electrolyte composition.

During the third quarter we have

- o Developed an improved cell design which permit long term storage tests.
- o Conducted stability tests for sulfuryl chloride electrolyte with added chlorine and bromine.
- o Characterized the passivating film in these electrolyte with complex plane impedance.
- o Characterized the performance of cells built with added chlorine and added bromine at temperatures down to -20°C and current densities up to 30mA/cm².

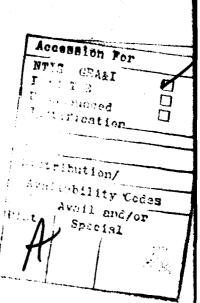
We have found that

- o Added bromine has an adverse effect on stability of lithium in sulfuryl chloride cells.
- o By elimination of solder seals a long term lithium corrosion rate in cells without additives of 5 mils per year is feasible.
- o Cells with added chlorine deliver greater coulombic capacities with, however, lower voltages than cells with added bromine at -20 C.
- o Calls with added bromine discharge approximately 500my above cells with added chlorine at current densities of 20 to 30 mA/cm.

Table of Contents

		Page Mumber
ı.	Introduction	1
11.	Anode Studies	3
	whose profites	, 3
	II.1 Corrosion	3
	II.2 Film Formation	9
III.	Cathode Studies	26
	III.1 Blectrolyte Additives	26
	III.2 Low Temperature Testing	30
	III.3 Cathode Composition Study	31
IV.	Future Work	35
IV.	Future Work	35





List	t of	. Fi	gu	Tel	ı
------	------	------	----	-----	---

		Page Mumber
1.	Design of Solderless Feedthrough/Fill Tube/Cell Cap	4
2.	Li/SO ₂ Cl ₂ +Br ₂ Cell Corrosion Rate Data	7
3.	Lithium Corrosion in a Li/SO2Cl2 Cell Without Additives	8
4.	Lithium Corrosion in a Cell With Added Cl ₂	10
5.	Complex Plane Impedance Spectrum of Li/SO ₂ Cl ₂ +Br ₂ 20 Rours After Activation	11
6.	Complex Plane Impedance Spectrum of Li/SO ₂ Cl ₂ -Br ₂ 68 Hours After Fill	12
7.	Complex Plane Impedance Spectrum of Li/SO ₂ Cl ₂ +Br ₂ 144 Hours After Fill	13
8.	Complex Plane Impedance Spectrum of Li/SO ₂ Cl ₂ +Br ₂ 163 Hours After Fill	14
9.	Change in Film Resistance and Thickness During Storage of Li/SO ₂ Cl ₂ +Br ₂	15
10.	Complex Plane Impedance Spectrum of Li/80 ₂ Cl ₂ Without Additives 2 Hours After Fill	17
11.	Complex Plane Impedance Spectrum of Li/802Cl2 Without Additives 19 Hours After Fill	18
12.	Complex Plane Impedance Spectrum of Li/80 ₂ Cl ₂ Without Additives 44 Hours After Fill	19
13.	Complex Plane Impedance Spectrum of Li/SO ₂ Cl ₂ Without Additives 20 Hours After Fill	21
14.	Complex Plane Impedance Spectrum of Li/SO ₂ Cl ₂ +Cl ₂ 2 Hours After Fill	22
15.	Complex Plane Impedance Spectrum of Li/SO ₂ Cl ₂ +Cl ₂ 19 Hours After Fill	23
16.	Complex Plane Impedance Spectrum of Li/SO ₂ Cl ₂ +Cl ₂ 45 Hours After Fill	24
17.	Schematic Cross Section and Description of 50mm Diameter Cell Used in Li/SO ₂ Cl ₂ +Cl ₂ 45 Hours After Fill	27
18.	Discharge Curves of Li/SO ₂ Cl ₂ Test Cells	28

List Of Tables

		Page Mumber
1.	Design Characteristics for Second Generation Cells employed in Anode Stability Studies	5
2.	Capacities (in Ah) of Li/ 80_2 Cl ₂ Cells at 20 mA/cm ² and 30 mA/cm ² for Br ₂ and Cl ₂ Additives	29
3.	Capacities (in Ah) of Cells Run With Various Electrolyte at 25°C and -20°C	32

I. Introduction

Batteries built with an inorganic catholytes (e.g., thionyl chloride and sulfuryl chloride) are very attractive for military applications on the basis of their high demonstrated energy density, and high discharge rate capability when compared with organic electrolyte lithium cells. By far the greatest attention has been given to the lithium-thionyl chloride (Li/SOCl₂) system. Cells and batteries have been demonstrated with energy densities in excess of 600 Wh/kg (1).

Despite the impressive levels of performance demonstrated with Li/SOC1₂ wide spread deployment has not yet occurred principally due to unresolved safety issues. One of the probable causes for explosion of Li/SOC1₂ cells during overheating either as a result of short circuiting or an external heat source is the reaction between lithium and sulfur (2), which is formed by cell discharge according to the discharge reaction (3)

$$4Li + 2SOC1_2 = 4LiC1 + 80_2 + 8$$
 (1)

In this regard $\text{Li}/80_2\text{Cl}_2$ may be a fundamentally safer system as no sulfur is formed in the discharge reaction (4)

$$2Li + 80_2C1_2 = 2LiC1 + 80_2$$
 (2)

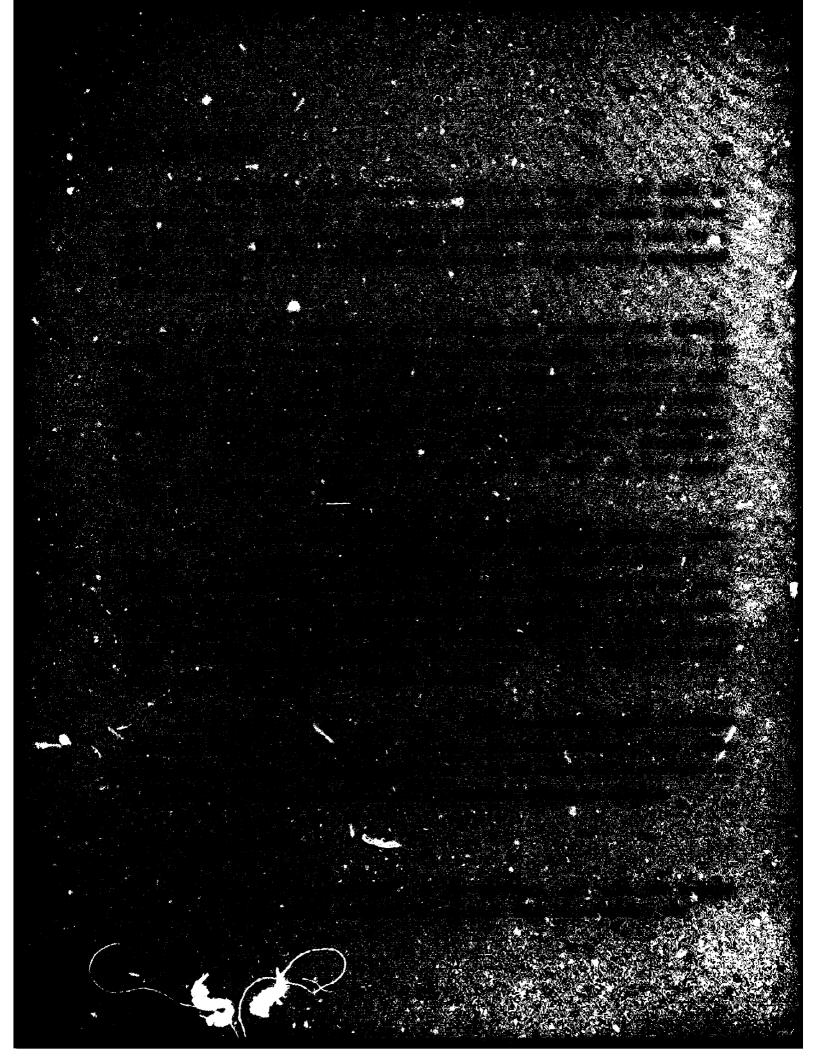
Development of potentially safer Li/80₂Cl₂ cells for military applications will require the demonstration of cells with a long shelf life and performance which at least approaches that of Li/80Cl₂. The former requirement is principally a function of controlling the rate of lithium corrosion. The latter requirement entails optimisation of the anode with respect to voltage delay and the cathode with respect to voltage and capacity in the range of 1 to 20 mA/cm² at temperatures down to -40°C.

The scope of the present contract encompasses investigation and improvement of both anode stability and the performance of both electrodes.

Previous work in the first and second quarters of the contract has established

- An intrinsically low rate of lithium corrosion (less than 1 mil per year, mpy) in sulfuryl chloride electrolyte
- A much higher in cell corrosion rate (100 to 50 mpy)
 which we ascribe to impurities in the components of cell construction
- Substantial voltage delay after storage which is substantially reduced by use of a bromine additive to the electrolyte
- Superior room temperature positive electrode operating voltage and capacity with added bromine and to a lesser extent added chlorine
- The conductivity and density of sulfuryl chloride electrolyte.

Work in the third quarter described herein has focused on lowering the in cell corrosion rate, establishing the preferred cathode composition and determining the performance characteristics of Li/SO₂Cl₂ cells at temperature of -20°C and below.



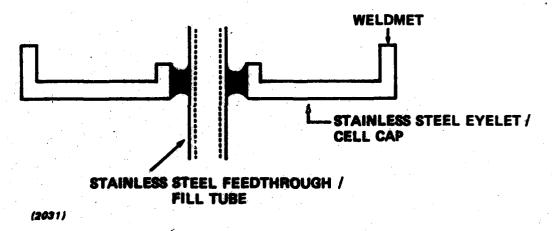


Figure 1 Design of Solderless Feedthrough/fill tube/Cell Cap

TABLE 1

Design Characteristics for Second Generation Cells employed in Anode Stability Studies

- 304 stainless steel case with integral glass to metal seal
- Positive grounded
- 90% Shawinigan Black, 10% PTFE cathode, 0.02" thick, nickel Exmet supported
- 0.002" negative nickel sheet current collector
- 0.01" lithium foil pressed to both faces of the current collector
- 0.004" porous Teflon insulator between the anode and the case
- Cell TIG welded

corrosion rate shortly after fill (approximately 20 hours) is about 25% of our previous best data reported in last quarter. However, the data do not show the previously observed exponential decrease in corrosion with time. Rather the corrosion rate appears to be linearly decreasing and has reached a value of 32 mpy 175 hours after cell activation.

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This value is close to what was previously observed with a soldered feedthrough. This suggests in the case of the bromine additive at least that the long term corrosion rate may be intrinsic to the chemistry and not the level of purity.

The data in Figure 2 also may explain why cells with added bromine show less voltage delay after storage. If the lithium surface continues to undergo a high rate of corrosion then the formation of a thick passivating film may be inhibited which would result in less voltage delay.

In Figure 3 corrosion data for a Li/SO₂Cl₂ cell without any additive is given. In this case the data do show a clear exponential decay. Although the initial corrosion rate is slightly higher than that shown in Figure 2, by 40 hours the corrosion rate has fallen to 32 mpy year whereas with the bromine additive the corrosion rate is 126 mpy.

The data in Figure 3 show an approximate three-fold decrease in lithium corrosion when compared to results reported in the first quarterly report. If the trend in Figure 3 continues we expect the long term (e.g. 500 hour) corrosion rate to fall below 5 mpy.

The markedly different behavior between cells with and without added bromine suggests that LiBr may be disrupting the LiCl lattice in the latter case and result in higher corrosion rate. This conclusion, however, probably over simplifies the situation as ampule experiments have shown a lower corrosion rate for lithium in the bromine containing electrolyte. Thus trace impurities may still be a problem in both Li/SO₂Cl₂ + Br₂ and unadulterated Li/SO₂Cl₂.

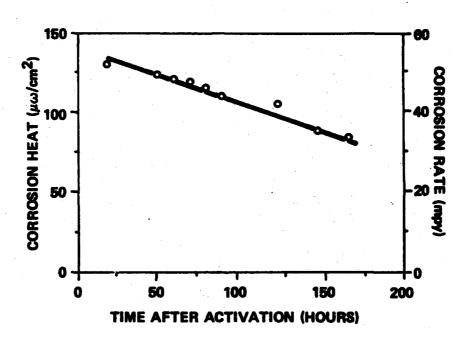


Figure 2 Li/SO₂Cl₂+Br₂ Cell Corrosion Rate Data
o 1.25 " Ø Cell, 1" Ø Electrodes
o Floating Double Faced Li Electrode
o 25°C, Positive SS Case

(2055)

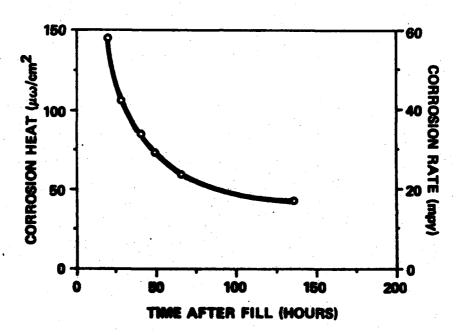


Figure 3

Lithium Correcton in a Li/80₂Cl₂ Cell without Additives
o 25°C
o 1.25 "Doell, 1" Ø Electrodes
o Double fased Anode
o Positive \$\$ case

(2006)

Finally we are measuring the rate of lithium corrosion in a cell with added chlorine. Data over the first 135 hours of testing are summarized in Figure 4. Qualitively the behavior of this cell is very similar to that of a Li/SO₂Cl₂ cell without additives. The corrosion rate at any time is slightly higher with added chlorine but in both cases a clear exponential decay is evident.

We would expect the similar data trends shown in Figure 3 and 4. Chlorine will always be present in sulfuryl chloride due to thermal decomposition

$$SO_2Cl_2 = SO_2 + Cl_2$$
 (3)

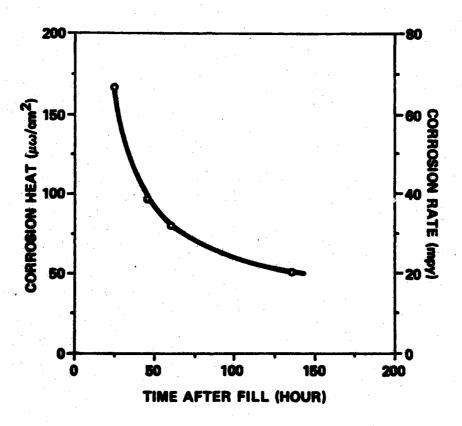
With added chlorine no unexpected products should form in the passivating crystal lattice. The slightly higher corrosion rate with chlorine addition probably indicates electrolyte contamination during chlorine addition.

The heat generation of all three cells is still being monitored. Now that we have apparently solved the feedthrough problem these cells will provide baseline data for improvements in anode stability.

II.2 Film Formation Studies

Complex plane impedance analysis on the three cells built for anode corrosion measurements is being simultaneously carried out. In Figures 5 through 8 the impedance spectra for the $\text{Li/80}_2\text{Cl}_2$ + Br_2 cell are given at intervals between 20 and 163 hours after activation. As has been previously observed the frequency at the maximum of the semicircle decreases with storage time and there is clear evidence by 163 hours of storage for the formation of a second lower frequency semicircle.

As has been previously observed in cells without additives both the film thickness and resistance increase with storage time. In Figure 9 both film resistance and thickness changes during storage are given; both continue to increase after 163 hours of storage.



Lithium Corrosion in a Li/SO₂Ci₂ Cell with Figure 4 Added Cl₂ o 25°C

o 1.25 "Ø cell, 1" Ø Electrodes

o Double faced Anode

o Positive SS Case

(2067)

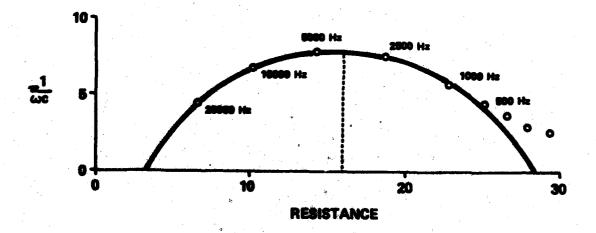


Figure 5 Complex Plane Impedence Spectra of Li/SO $_2$ Cl $_2$ +Br $_2$ 20 hours after activation
Rfilm = 25 ohms, 13 X 10 7 ohm cm
Cfilm = 5.1 μ F
Thickness = 19.1

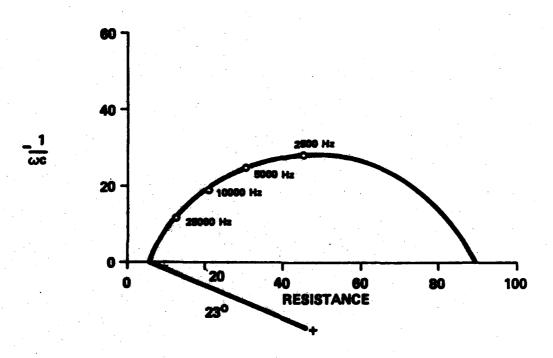
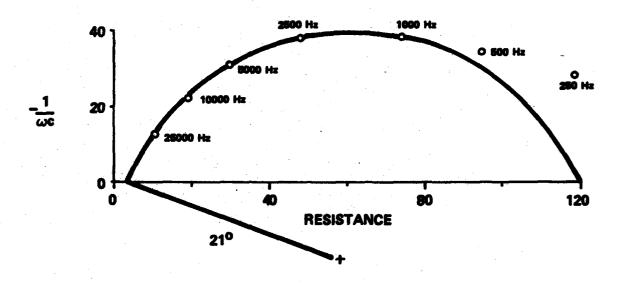


Figure 6 Complex Plane Impedence Spectrum of Li/SO $_2$ Cl $_2$ +Br $_2$ 68 hrs. after fill R_{film} = 86 ohms, 25X10⁸ ohm-cm C_{film} = 2.83 μ F Thickness = 345A $^\circ$



Complex Plane Impedence Spectrum of Li/SO₂Cl₂+Br₂ Figure 7 144 hrs. after fill R_{film} = 117 ohms, 28×10⁷ ohm-cm C_{film} = 2.3 μ f Thickness = 420 A^o

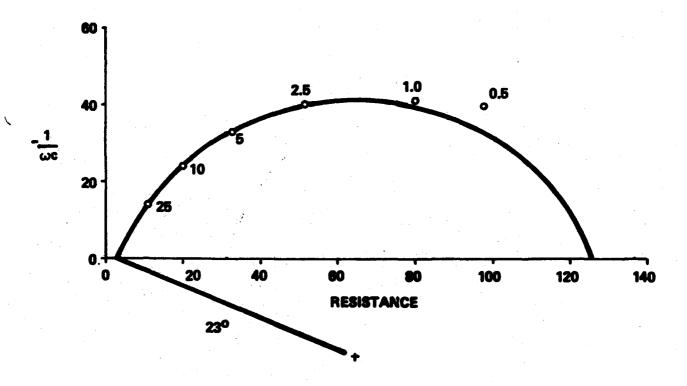


Figure 8 Complex Plane Impedence Spectrum of Li/SO $_2$ Cl $_2$ +Br $_2$ 163 hrs. after fill $R_{film} = 123~\Omega,~24\times10^7~\Omega - cm$ $C_{film} = 2.0~\mu~F$ Thickness = 510 Ω

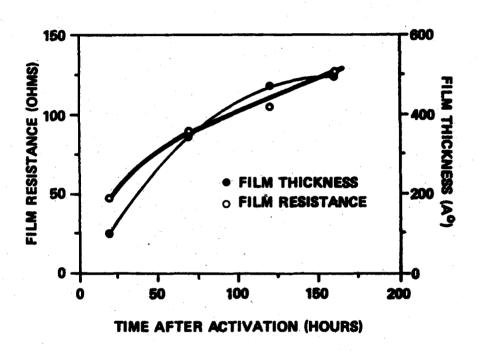


Figure 9 Change in Film Resistance and Thickness During Storage of Li/SO₂Cl₂+Br₂

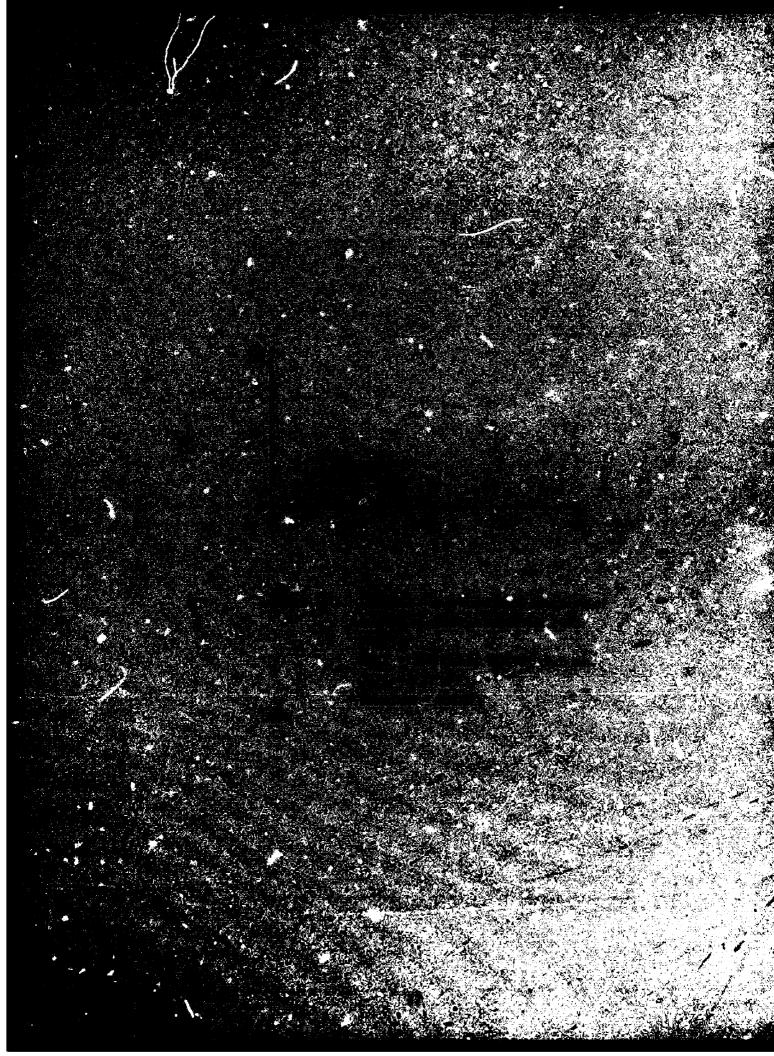
(2058)

The film resistivity is in fact considerably greater than that previously reported to Li/SO₂Cl₂ without additives. As can be seen from the numerical data in Figure 5-8 after the initial 20 hour measurement the resistivity is essentially constant at approximately 25 x 10⁷ ohm-cm. This compares with the previously measured film resistance 8.2 x 10⁷ ohm-cm after 412 hours of storage of a cell with a solder seal and no additive. It is probable that the lower film resistance previously measured indicates film doping with heavy metal ions which would also be expected to increase the corrosion rate.

A final observation from the data in Figures 5-8 is that the high frequency intercept of the semicircle with the real axis is essentially invariant (approximately 3 ohms) between 20 and 16, hours of storage. Previous solder sealed cells without additives had shown an increase of this intercept with storage time. This was attributed to an accumulation of non-adherent LiCl crystals adjacent to the anode increasing circuit resistance and hence the high frequency intercept. The constant intercept observed in the present work is most probably a result of the lower corrosion rate. It is also possible that the corrosion products remain adherent to the lithium possibly affording greater anode protection.

In Figures 10-12 complex plane impedance spectra for the cell with no additives are given. The data cover the period between 2 and 44 hours after activation. The following features are noted with regards to the data.

- Film resistivity, as was the case with Li/80₂Cl₂ + Br₂; is considerably greater than observed in the first quarter work.
- e Film thickness is much lower for equivalent storage periods than observed in the first quarter.
- The high frequency intercept appears to be constant with storage time.



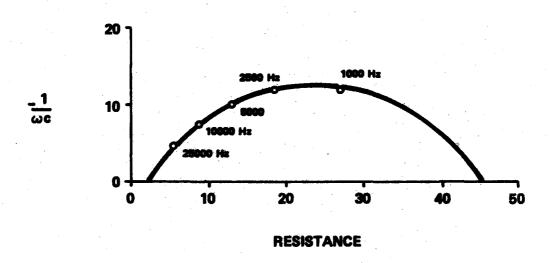


Figure 11 Complex Plane Impedence Spectrum of Li/SO $_2$ Cl $_2$ without Additives 19 hrs. after fill Rfilm = 43 ohms, 37X10 7 ohm cm Cfilm = 8.43 μ F Thickness = 116A 0

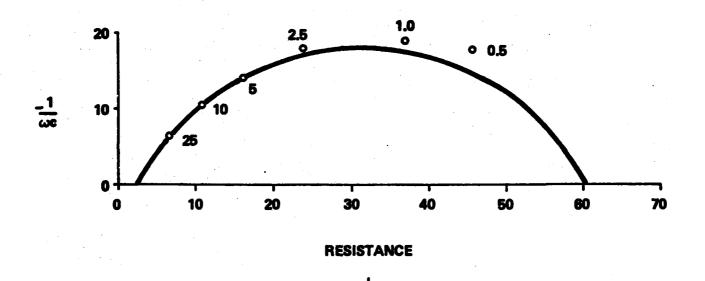


Figure 12 Complex Plane Impedence Spectrum of Li/SO $_2$ Cl $_2$ without Additives 44 hrs. after fill Rfilm = 58 ohm, 25 \times 10 7 ohm—cm Cfilm = 4.17 μ F Thickness = 230 \wedge 0

(2052)

• The frequency at the maximum of the semicircle decreases with storage time.

The cell has not been on test for a sufficient period to establish long term trends. The initial data are, however, encouraging with regard to improved anode performance as thinner films should result in less voltage delay.

An interesting though not yet fully understood result was obtained in our investigation of Li/SO₂Cl₂ anode film in the absence of additives. The cell under test is the second one built in this reporting period. The first cell for unknown reasons failed after 20 hours of testing. Prior to failure limited complex plane impedance and calorimetric was obtained and is summarised in Figure 13. What is noteworthy about the data is

- The cell corrosion rate at 20 hours is approximate 75% of that of the second cell.
- The film resistance and thickness are both considerably greater and the film resistivity less.
- The center of the semicircle lies much closer to the real axis than we have previously observed.

The final set of film studies carried out this quarter were on the cell with added chlorine. Complex plane impedance spectra for this cell are given in Figures 14-16 between 2 and 45 hours after activation.

The data differ radically from the cases summarized in Figures 5-8 and 10-12. For a given storage time film thickness is nearly double that of the cell without additives. Film resistivity on the other hand is much lower

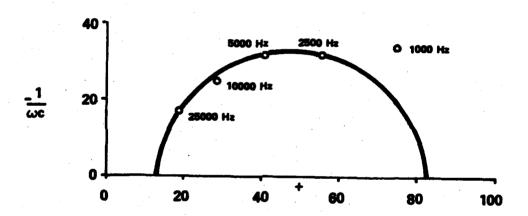


Figure 13 Complex Plane Impedence Spectrum of Li/SO $_2$ Cl $_2$ Without Additives 20 hrs. after fill $R_{film} = 68 \text{ ohms, } 8\times10^7 \text{ ohm cm}$ $C_{film} = 1.21 \ \mu \text{ F}$ Thickness = 806A^0 Corrosion Rate = $88 \ \mu\omega/\text{cm}^2$, $36 \ \text{mpy}$ (2061)

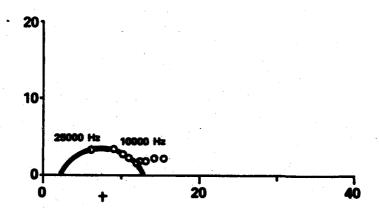
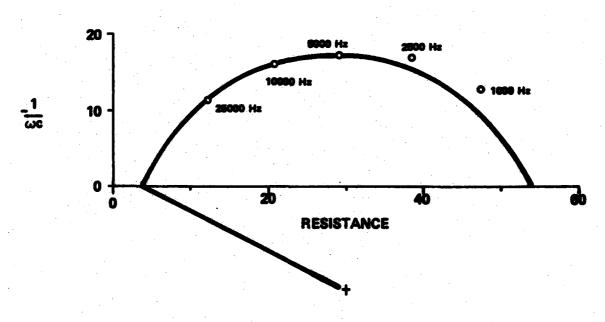


Figure 14 Complex Impedence Spectrum of Li/SO $_2$ Cl $_2$ +Cl $_2$ 2 hrs. after fill R_{film} = 11 ohm, 3X10 7 ohm cm C_{film} = 2.67 μ F Thickness = 366A $^\circ$

/22001



Complex Plane Impedence Spectrum of Li/SOCI₂+CI₂ 19 hrs, Figure 15 after fill R_{film} = 50 ohms, 9X10⁷ ohm om C_{film} = 1.83 μ F Thickness = 556A⁰ (2080)

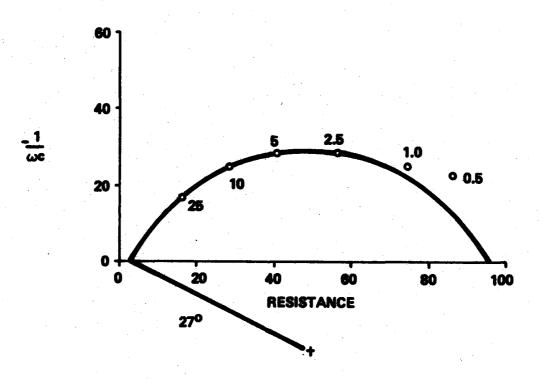


Figure 16 Complex Plane Impedance Spectrum of Li/SO $_2$ Cl $_2$ +Cl $_2$ 45 hrs. after fill R_{film} = 93 ohms, 13X10 7 ohm cm C_{film} = 1.45 μ F Thickness = 705A $^\circ$

(2059)

possibly indicating metal atom doping of the film. Further complex plane analysis over a longer time span will be required to determine if these differences persist. In any event the high frequency intercept is not changing in agreement with the lower corrosion rate when compared to earlier work.

III. Cathode Studies

Under the heading of cathode studies three areas of interest were investigated: (i) electrolyte additives, (ii) low temperature performance, (iii) cathode composition.

The test vehicle for these studies consisted of 2 inch hermetically sealed cells with both electrodes floating as shown in Figure 17. The anodes were composed of 20 mil Li pressed on 5 mil nickel mesh; the cathodes were composed of approximately 0.35 g of a Shawinigan Black (SB)/PTFE mixture pressed on 11 mil Ni mesh to a uniform thickness of 0.020 in. Five mil Manninglas was used as the separator. Double distilled SO₂Cl₂ was used in the formulation of all electrolytes.

III.1 Electrolyte Additives

The addition of LiAlCl₃Br to 80_2 Cl₂/LiAlCl₄ electrolyte was shown in the last quarter to out perform all other electrolyte tested at 10 mA/cm^2 . Cells using the bromide additive were compared to cells using 80_2 Cl₂/l.5 M LiAlCl₄ (standard electrolyte); the bromide cells discharged with higher capacities and at higher voltages. A comparison between cells using the standard electrolyte plus Cl₂ and cells using the bromide additive was also made, the results again demonstrated the bromide additives beneficial effects. This quarter additional runs comparing cells w/Cl₂ added vs. cells w/Br' added were made at 20 mA/cm^2 and 30 mA/cm^2 .

Eight 2 inch cells as described above were fabricated using 90% SB/10% PTFE as the cathode mix. The electrolytes used were 80_2 Cl₂/1.0 M LiAlCl₄/0.5 M LiAlCl₃Br and 80_2 Cl₂/1.5 M LiAlCl₄/0.5 M Cl₂. Four cells were discharged at 20 mA/cm², 3 cells at 30 mA/cm² (one cell leaked upon filling). The results are seen in Table 2 and Figure 18.

From the table and figure the ${\rm Cl}_2$ cells appear to deliver at 20 mA/cm² a higher capacity. At 30 mA/cm² the difference may be attributable to scatter. The bromide additive cells still operate at a higher voltage, but

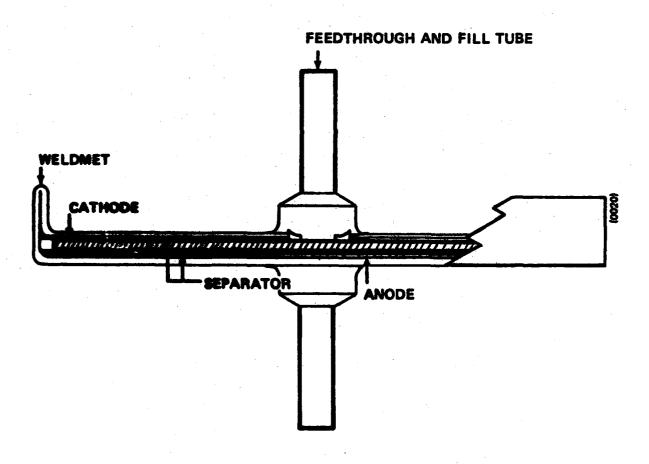


Figure 17 Schematic Cross Section and Description of 50mm diameter Cell used in Li/SO₂Cl₂ Studies

CATHODE: 90/10 Shawinigan Black/PTFE 0.35g pressed onto

expanded Ni screen

ANODE: 20mil Lithium foil pressed onto expended Ni screen

SEPARATOR: 5 mil Menniingles INSULATOR: 10 mil Telfon sheet

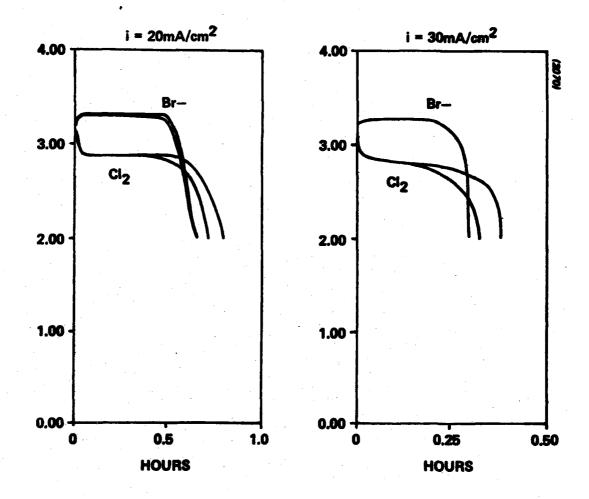


Figure 18 Discharge Curves of Li/SO₂Cl₂ Test Cells
Run at 20 and 30 mA/cm² with LiAlCl₃Br Added and Cl₂ Added

TABLE 2

Capacities (in Ah) of Li/80₂Cl₂ Cells at 20 mA/cm² and 30 mA/cm² for Br₂ and Cl₂ Additives At Room Temperatures

	so _{2C12}	80 ₂ C1 ₂ 1.5 m lia1C1 ₄ /0.5 m Cl ₂	
1	1.0 M Liaici4/0.5 M Liaici2Br2		
20 mA/cm ²	0.198	0.240	
	0.198	0.216	
30 mA/cm ²	0.139	0.144	
		0.176	

the higher ${\rm Cl}_2$ capacities are contrary to the trends observed at 10 mA/cm². At 10 mA/cm² the ${\rm Cl}_2$ cells behaved identically to the cells using the standard electrolyte (lower capacity than ${\rm Br}_2$ cells) except for the higher initial voltage. From this observation one might expect comparable results at 20 and 30 mA/cm². This is not the case as seen in Table 2. Apparently the addition of ${\rm Cl}_2$ facilitates more complete utilization of the cathode at 20 mA/cm² than the addition of bromide. How ${\rm Cl}_2$ more efficiently utilizes the cathode is not known but possibly it may affect the solubility of the reaction products or cause the discharge to proceed via a more efficient mechanism.

A comparison of Cl_2 cells vs Br_2 cells at additional current densities is planned for the coming months.

III.2 Low Temperature Testing

Most of the work presented to date was from discharge data accumulated at 25°C. Cells were stored at 60°C and 40°C, but were discharged after they cooled to room temperature. All of our 25°C discharge data show the superiority of the Br₂ additive compared to Cl₂ or no additive at all.

This quarter discharge data were obtained at -20°C to investigate what effect low temperatures have on cell performance.

Four kinds of electrolyte were investigated in this experiment

 $80_2\text{Cl}_2/1.5$ M LialCl4/0.5 M Cl2 $80_2\text{Cl}_2/1.5$ M LialCl4/0.5 M Cl2 $80_2\text{Cl}_2/1.0$ M LialCl4/0.5 M LialCl3^{Br} $80_2/\text{Cl}_2/1.5$ M LialCl3^{Br}

The lithium salts were obtained from a commercial laboratory, the ${\rm Cl}_2$ was added employing a double gas scrubbing apparatus. Cells were discharged at 10 mA/cm² at -20°C and at 25°C for comparison. Since we have no way in this experiment to determine the day to day variability, only comparisons of cells fabricated and run on the same day will be made.

From the results seen in Table 3 one startling result is apparent, at -20° C the bromide additive cells have lower capacities then cells using standard electrolyte. Also since there does appear to be no significant differences between Cl_2 added cells and the standard cells at -20° C, we can imply that the Cl_2 additive cells also have better capacities than the bromide additive cells at -20° C. This trend is opposite to the results evident at 25° C in this experiment and what we have observed in past experiments at 25° C.

The reactions involving bromine additive are more sensitive to low temperature than the reactions taking place in the cell in the presence of Cl₂, or in the absence of any additives.

In addition two cells were run using $SO_2Cl_2/1.5$ M LiAlCl₃Br. The results seen in Table 3 do not appear promising as the capacities in both cells (one at 25°C and one at ~20°C) are below normal for this cell chemistry. The operating voltages though in these cells were 100 mV higher than cells using a LiAlCl₄/LiAlCl₃Br mixture and 500 mV higher than standard electrolyte or Cl_2 added electrolyte cells. More testing on the optimum LiAlCl₃Br concentration is planned.

Additional testing comparing these four electrolytes at -20°C is planned, as well as testing at -40°C. If cells using the $\rm Br_2$ additive run at low temperatures continue to demonstrate poor performance than $\rm Cl_2$ added and standard electrolyte cells, this additive may prove unacceptable in batteries performing in this environment.

III.3 Cathode Composition Study

Most of the data obtained to date under this contract was from cella using 90% Shawinigan Black/10% PTFE binder as cathode material. This study was devised to compare the 90/10 cathode to the 95/5 cathode. A 2³ factorial design experiment was developed for this study. The two additional factors

TABLE 3

Capacities (in Ah) of Cells Run with various Electrolytes at 25°C and -20°C

		Standard	C12	Bromide	Bromide
Run	Temp.	Electrolyte	Added	Additive (0.5)	Additive (1.5)
1	25°C	0.360	0.390		
			0.447		
2	25°C	0.303		0.441	0.285
				0.348	
3	-20°C	0.422		0.270	
				0.315	0.300
4	-20°C	0.353	0.316		·
	· .	0.294	0.341		
5	-20°C	0.388	0.347		
			0.347		
•	-20° 0	0.316		0.244	
•		0.338		0.264	

are current density and the bromide additive. The experimental design and the data obtained are as follows:

1	-	-	-	A.	Cathode composition	+ 95% SB/5% PTFE
a	+	-				- 90% SB/10% PTFE
þ	-	=	-	В.	Additive	+ w/B ₂ -
ab	• +	+	-			- w/o B2
c	-	-	+	C.	Current density	+ 2 mA/cm ²
ac	. +	-	+			- 10 mA/cm ²
abc	+	+	+			

	Results	
	Capacity (Ah)	Total Watt-Hours
. · 1	0.447	1.90
•		1.36
4	0.804	2.45
b	0.540	1.86
ab	0.930	3.21
c	0.789	2.60
AC	1.010	3.33
bc	0.710	2.56
abc	0.908	3.27

Mo statis ical significance can be assigned to any of the factors until a replicate is performed, but the performance of cells with the 95/5 cathode is much better than those with the 90/10 cathode as shown in the above data. Wherever the 95/5 cathode was used (a plus (+) in column A) the capacity and the total watt-hours are at least 20% higher than its counterpart using

90/10. This data is contrary to previous work using sealed jar cells, in those experiments 90/10 was shown to be better. The other two factors exhibit predictable results. Lower current density = higher capacity; presence of additive = higher capacities.

Additional runs of this experiment are planned to determine if this initial trend in cathode composition is statistically significant.

IV. Future Work

Now that we have developed a long life cell design with at least improved anode stability we plan to focus our attention in the fourth contract quarter on

- Investigation of means of improving anode stability and minimizing voltage delay. Three possible means of doing this are cyanoacrylate coating, vinyl chloride coating and prepassivation of the anode in pure thionyl chloride.
- Reinvestigate design variables which may effect anode stability. Some work in this area was carried out in the second quarter on cells with a solder joint between the case and feedthrough. The instability of this joint requires further study of the proper choice of grounding. In addition the use of a PTFE insulator between the anode and case may not be advisable as these two components react.
- e Ampule studies of lithium foils in sulfuryl chloride electrolytes doped with possible cell contaminants such as water and heavy metal ions. The great difference between cell and ampule results to date strongly indicates a contaminant problem. Ampule studies with known contaminant levels will provide an efficient means of identifying which spieces must be excluded from the cell.

Most of our attention will be directed at resolving the anode problem. We do plan, however, to continue parametic cathode optimization and initiate limited performance characterization in simulated Army use such as a laser designator battery discharge regime. Finally we will carry out spectroelectrochemical studies of $\text{Li/SO}_2\text{Cl}_2$ speciation during discharge and reversal. The equipment and techniques for this have already been perfected under a Navy contract at Gould for study of Li/SOCl_2 reactions.

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